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# Photo-induced changes in the complex index of refraction in conjugated polymer/fullerene blends

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We report steady-state photo-induced absorption (PIA) and photo-induced reflectance (PIR) in films of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) and poly[2,5-bis cholestanoxy-1,4 phenylene vinylene] (BCHA-PPV) blended with fullerenes. Absorption from the metastable charge-transferred state is probed by PIA; the modulated absorption spectrum causes changes in the real part of the index of refraction,  $\Delta n$ , which can be measured directly by PIR. The charge transfer gives rise to pronounced features in  $\Delta n$ , including vibrational structure in the mid-infrared, and broad spectral windows with negative  $\Delta n$  in the mid- and near-infrared. Our measurements over a wide spectral range (0.05 eV–1.9 eV) allow quantitative comparison of  $\Delta n$  obtained from PIR with that obtained from Kramers–Kronig transformation of the PIA data. We find good agreement throughout the infrared, indicating that our method for measuring  $\Delta n$  is useful as an analytical tool for optical characterization and for prediction of optical spectral ranges for nonlinear optical response. © 1998 American Institute of Physics. [S0021-9606(98)52304-5]

## I. INTRODUCTION

The recent discovery of photo-induced electron transfer from  $\pi$ -conjugated polymers onto buckminsterfullerene ( $C_{60}$ ) has generated considerable interest because of its implications in both pure and applied areas of research. Ultrafast spectroscopic studies<sup>1</sup> show that the initial charge transfer occurs within the first 300 fs following excitation of the polymer and that the system quickly relaxes to a metastable state with the electron on the fullerene and a positive charge on the polymer. Steady-state photo-induced absorption<sup>2,3</sup> and photoconductivity<sup>4</sup> measurements indicate that recombination from the charge-separated state is metastable and thermally activated, with a lifetime that varies from milliseconds at liquid nitrogen temperature to microseconds at room temperature.

Because of the nearly instantaneous response of the system to illumination and because of the tunability of the decay dynamics by fullerene concentration,<sup>5</sup> conjugated polymer/fullerene blends are promising candidates for nonlinear optical (NLO) applications. Because the NLO response arises from excitation from the metastable charge-transferred excited state, total fluence within the decay time for back charge transfer is the relevant parameter. Pulsed laser experiments have already shown<sup>5</sup> that these blends can be used for ultrafast holography with good diffraction efficiency, indicative of an incoherent third-order NLO susceptibility of the

order  $10^{-8}$  esu. Larger values are anticipated from longer pump pulses and from probing at wavelengths where  $\Delta n$  is largest. Thus, a thorough understanding of the mechanism for the nonlinearity is necessary and spectral windows for maximum response must be identified before materials can be optimized for NLO applications such as holography or optical limiting.

In this work, we present steady-state measurements of the photoinduced absorption (PIA) and photoinduced reflectance (PIR) spectra in polymer/fullerene blends using poly[2,5-bis cholestanoxy-1,4 phenylene vinylene] (BCHA-PPV) and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV), blended with the fullerenes,  $C_{60}$  and phenyl[5,6] $C_{61}$ -butyric acid cholesteryl ester ([5,6] PCBCR), respectively. Our measurements, carried out over a broad spectral range (0.05 eV–1.9 eV) on a single instrument, allow us to compute the photo-induced changes in the complex refractive index,  $\Delta N = \Delta n + i\Delta\kappa$ , where  $\Delta\kappa$  is related to the change in the absorption coefficient [ $\Delta\alpha = (2\omega/c)\Delta\kappa$ ]. Both  $\Delta n$  and  $\Delta\kappa$  are of the order  $10^{-3}$  at liquid nitrogen temperature with a pump intensity of only 50 mW/cm<sup>2</sup>. The refractive index,  $n$ , changes in response to the induced absorption,  $\Delta\alpha$ , as predicted by the Kramers–Kronig (KK) integral relations.

## II. EXPERIMENT

Thick films (15  $\mu\text{m}$ ) of the polymer/fullerene blends were drop-cast from xylene solution onto polished KBr substrates for PIA and PIR measurements. MEH-PPV was

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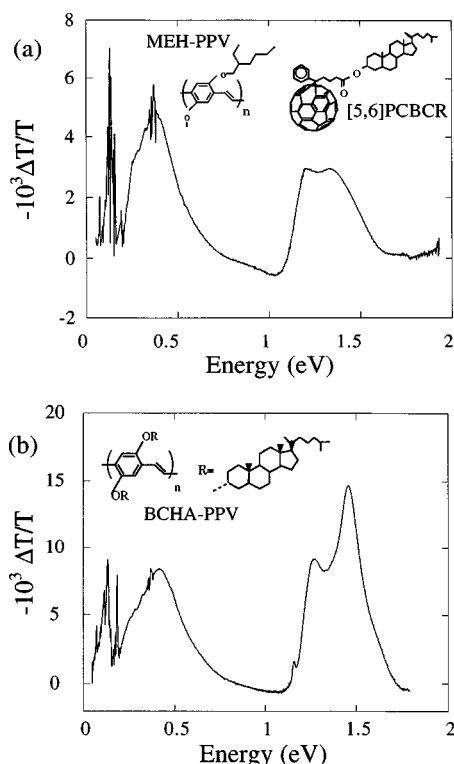


FIG. 1. Photo-induced absorption spectra of (a) MEH-PPV/[5,6]PCBCR in a 10:1 weight ratio and (b) BCHA-PPV/C<sub>60</sub> in a 20:1 weight ratio. The measurements were done with the samples at 80 K, illuminated with 50 mW/cm<sup>2</sup> of 2.41 eV radiation from an Ar<sup>+</sup> laser. The molecular structures are shown in the inset.

blended with [5,6]PCBCR in a 10:1 weight ratio (1 fullerene per 49 monomer units), and BCHA-PPV was blended with C<sub>60</sub> in a 20:1 weight ratio (1 fullerene per 17 monomer units). The chemical structures of these molecules are shown in the insets of Fig. 1. MEH-PPV and BCHA-PPV were obtained from UNIAX Corporation and used as received. The synthesis of [5,6]PCBCR is described elsewhere.<sup>6</sup> Thin films (100 nm) of the same materials were spin-cast for linear absorption measurements. Our 15 μm thick films showed excellent surface quality and little scattering below the  $\pi$ - $\pi^*$  absorption edge of the polymer. Linear reflectance and absorption measurements on the films confirm that electron transfer does not occur in the ground state and that the spectrum is a simple superposition of spectra from the two components. These data are consistent with earlier studies that have shown no ground state mixing of electronic wave functions in such composites.<sup>7,8</sup> In particular, there is negligible absorption at energies below the  $\pi$ - $\pi^*$  absorption in the polymer.

PIA and PIR measurements were made with the sample at 80 K in dynamic vacuum on the cold finger of a liquid nitrogen cryostat. Difference spectra were recorded with a Nicolet Magna-750 FTIR spectrometer by first exposing the sample to the 2.41 eV beam from an argon ion laser for ten seconds and then blocking the laser beam for 10 s. Typically 50 cycles gave an adequate signal to noise ratio in the appropriate quantity,  $\Delta T/T$  or  $\Delta R/R$ . PIA measurements were

made with the sample held at a 45° angle to the pump beam and to the probe beam, while PIR measurements were made with both the pump and probe beams at near-normal incidence. Care was taken to adjust the laser power to account for the different geometry and maintain a constant pump intensity of 50 mW/cm<sup>2</sup>.

### III. RESULTS AND DISCUSSION

#### A. Photo-induced absorption

The steady-state photoinduced absorption spectrum for the MEH-PPV/[5,6]PCBCR composite between 0.05 eV and 1.9 eV is shown in Fig. 1(a). The molecular vibrational modes made infrared-active by the charge separation are between 0.05 eV and 0.2 eV. Charges on the polymer chain change the local symmetry of the vibrational modes and induce coupling of formerly Raman-active modes to the optical field by creating a transition dipole. Also evident are broad electronic absorptions peaking at 0.37 eV, 1.2 eV, and 1.35 eV. From previous studies on these and related materials, we can readily identify the peaks at 0.37 eV and 1.35 eV as the low-energy (LE) and high-energy (HE) features associated with the charge on the polymer chain.<sup>9-12</sup> Similar absorption peaks are seen upon chemical doping of similar materials and are the result of structural relaxation of the polymer chain in response to the electron transfer. Distortion of the positively charged chain from its neutral state creates localized electronic states within the  $\pi$ - $\pi^*$  energy gap, and electronic transitions between these localized states and the extended states in the  $\pi$  and  $\pi^*$  bands are observed.<sup>10-12</sup>

The peak at 1.2 eV represents absorption by the fullerene anion from the lowest unoccupied molecular orbital (LUMO) of the ground state molecule, now occupied by the transferred electron, to the next higher level (LUMO+1). The LUMO level in [5,6]PCBCR is analogous to the  $T_{1U}$  LUMO level in C<sub>60</sub>, which shows a distinctive peak in the photo-induced absorption at 1.15 eV in the BCHA-PPV blend and in blends with other conjugated polymers.<sup>13,14</sup> The 1.2 eV transition seen here has been previously identified in blends of the [6,6] isomer of PCBCR with poly(3-octyl-thiophene) (P3OT).<sup>15</sup>

The PIA spectrum of the BCHA-PPV/C<sub>60</sub> blend [Fig. 1(b)] also shows the signatures of intermolecular charge transfer. The vibrational structure in the mid-IR, together with the peaks at 0.4 eV and 1.25 eV are characteristic of the charged polymer chain, and the conspicuous peak at 1.15 eV is the LUMO→LUMO+1 transition of the fullerene anion. In addition to the three electronic absorptions indicative of the charge transfer, the BCHA-PPV blend has a strong near-IR peak at 1.45 eV, characteristic of the triplet-triplet absorption in PPV derivatives. The magnitude of this absorption band increases almost linearly ( $\sim I^{0.91}$ ) with pump intensity in contrast to the square-root intensity dependence ( $\sim I^{0.52}$ ) of the 1.25 eV peak which is characteristic of bimolecular recombination of the charge-transferred species. Apparently, some fraction of the primary photoexcitations undergo ultrafast charge transfer while the rest either decay directly from the singlet state or cross into the manifold of

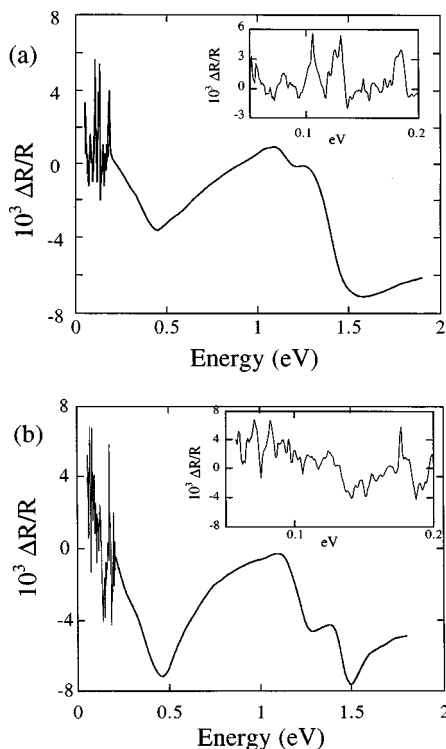


FIG. 2. Photo-induced reflectance spectra of the polymer/fullerene composites under conditions identical to those in the PIA measurement. The MEH-PPV/[5,6]PCBCR blend (a) shows two near-IR peaks associated with the charge transfer, but the BCHA-PPV/C<sub>60</sub> blend (b) shows a third peak associated with the triplet state. The insets show details of the mid-IR features associated with the IRAV modes.

triplet states on the nanosecond time scale. The bulky sidechains on the BCHA-PPV may act to dilute the fullerene and limit the spatial overlap between the wave function of the photoexcitation on the polymer and the fullerene. The smaller fraction of charge-transferred excitations for BCHA-PPV/C<sub>60</sub> has been previously observed in ultrafast studies as well<sup>16</sup> where the early-time decay of the PIA signal shows significant contribution from the primary excitations during the first several picoseconds, after which the charge-transferred species becomes dominant. In MEH-PPV/C<sub>60</sub>, on the other hand, the smaller sidechains do not inhibit the charge-transfer, and the initial decay occurs within the first picosecond.

## B. Photo-induced reflectance

While the PIA tracks the change in the absorption coefficient,  $\Delta\alpha$ , the PIR of the MEH-PPV/[5,6] PCBCR and BCHA-PPV/C<sub>60</sub> blends, shown in Figs. 2(a) and 2(b), respectively, tracks the change in the real part of the refractive index,  $\Delta n$ . Below 0.2 eV, as seen in the insets, the spectra are dominated by sharp features from the IRAV modes. Both PIR spectra show zero crossings near 0.2 eV and local minima near 0.45 eV. These two features derive from the mid-IR features in the PIA, with strong IRAV modes and a broad electronic absorption. Near 1.1 eV, the spectra have local maxima where the rising edge of the near-IR absorption cancels the contributions from the mid-IR features. At

slightly higher energy, both spectra show a weaker peak that derives from the change of slope of the PIA spectrum. In the MEH-PPV blend, the crossover from the fullerene absorption to the polaron or bipolaron absorption causes the shoulder in the PIR, while in the BCHA-PPV blend, the polaron/bipolaron and triplet absorptions give rise to the observed shoulder. In both cases, the PIR is negative above 1.3 eV as a result of the contributions from the PIA bands in the IR and the bleaching of the  $\pi-\pi^*$  absorption above 2.1 eV (not shown) that is familiar from other experiments.<sup>3,17</sup>

## C. Optical constants

The PIA and PIR spectra imply potentially useful changes in the optical properties of these blends at low pump intensities. For dielectric samples with reflectance  $R \ll 1$ , the PIA signal is proportional to the change in the absorption coefficient,  $\Delta\alpha$ ,

$$\frac{-\Delta T}{T} \approx d\Delta\alpha, \quad (1)$$

where  $d$  is the film thickness, and  $\Delta\alpha$  can, in general, include excited-state absorption as well as bleaching of ground-state transitions. The associated PIR spectrum can be analyzed by starting with Fresnel's equation for reflectance at normal incidence<sup>18</sup>

$$R(n, \kappa) = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}. \quad (2)$$

Differentiation with respect to  $n$  and  $\kappa$  gives the fractional modulated reflectance<sup>19</sup>

$$\frac{\Delta R}{R} = \frac{4(n^2 - \kappa^2 - 1)}{[(n+1)^2 + \kappa^2][(n-1)^2 + \kappa^2]} (\Delta n) + \frac{8n\kappa}{[(n+1)^2 + \kappa^2][(n-1)^2 + \kappa^2]} (\Delta \kappa) \quad (3)$$

In spectral regions of low absorption, the coefficient of  $\Delta\kappa$  is negligible,<sup>18</sup> so the modulated reflectance is proportional to  $\Delta n$ . Note that  $\Delta\kappa$  is related to  $\Delta\alpha$  by  $\Delta\alpha = (2\omega/c)\Delta\kappa$ , so  $\Delta n$  and  $\Delta\kappa$  are both of order  $10^{-3}$  in the IR.

In addition to the information on  $\Delta n$  obtained from PIR, measurement of the PIA over such a broad energy range allows one to compute  $\Delta n$  from the measured value of  $\Delta\alpha$ , thereby giving two independent determinations for comparison. The modulated index at a particular frequency  $\omega$ ,  $\Delta n(\omega)$ , is quite generally related to the modulated absorption over the entire spectrum by the Kramers–Kronig integral transformation<sup>20</sup>

$$\Delta n(\omega) = \frac{c}{\pi} P \int_0^\infty \frac{\Delta\alpha(\omega') d\omega'}{\omega'^2 - \omega^2}. \quad (4)$$

Several features of this integral are worth pointing out. First, the limits of integration are zero to infinity, so one must extrapolate beyond the limits of the measurement using data from complementary measurements. Second, the denominator of the integrand indicates that the most significant contribution comes from values of  $\Delta\alpha(\omega')$  very near the fre-

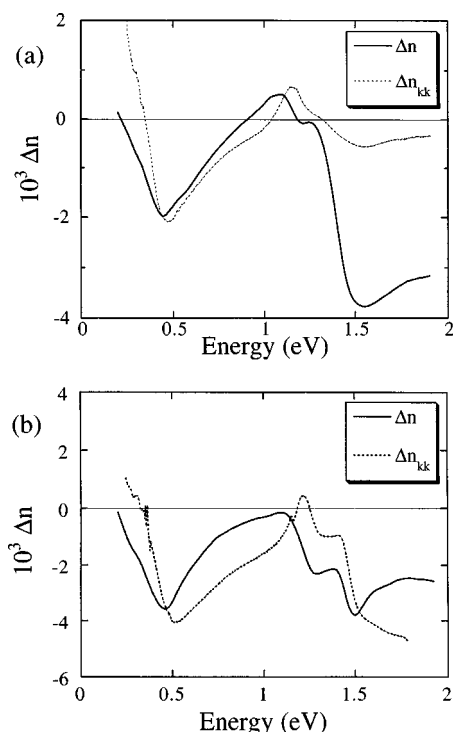


FIG. 3. Comparison of  $\Delta n$  measured by PIR (solid line) with the KK transformation of the PIA data (dashed line) (a) for MEH-PPV/[5,6]PCBCR and (b) for BCHA-PPV/C<sub>60</sub>.

quency  $\omega$ , with a minus sign for  $\omega' > \omega$ ; this is essentially the slope of the curve,  $\Delta\alpha(\omega')$ . Finally, remote spectral features with a large integrated area can influence the value of  $\Delta n$  whereas narrow bands and derivativelike features have little impact.

In Figs. 3(a) and 3(b), we plot the results of the KK integral transformation of the PIA data together with the value of  $\Delta n$  measured directly by PIR for MEH-PPV/[5,6]PCBCR and BCHA-PPV/C<sub>60</sub>, respectively. For the integration, we have used data from modulation spectroscopy measurements to extrapolate beyond the range of our instrument to account for the broad bleaching of the  $\pi$ - $\pi^*$  absorption of the polymer. This bleaching, caused by depletion of the  $\pi$  electron band following charge transfer and structural relaxation, has a strong effect on the value of  $\Delta n$  in the near-IR. Agreement between 0.5 eV and 1.3 eV is quantitatively good in both cases, indicating that our measurement of the PIR in this region is accurate. Deviation of the measured value from the KK result in the near-IR may be due to inhomogeneities at the surface of the sample, since PIR is more sensitive than PIA to thin layers at the surface.<sup>21,22</sup> Qualitatively, though, we see that the spectra agree over the full range shown, 0.2 eV through 1.9 eV, with good correspondence between features in the measured spectrum and those in the calculated spectrum.

#### IV. NONLINEAR RESPONSE

The changes in the steady-state optical spectra of polymer/fullerene blends are dominated by resonant effects which arise from excited-state absorption and are adequately

described by the Kramers–Kronig relations. However, because the index of refraction of the films can be changed by varying the pump intensity, the response can alternatively be described as a dynamic or incoherent nonlinearity,  $\chi_{\text{inc}}^{(3)}$ .<sup>21</sup> This resonant nonlinearity can be measured directly by pulsed laser experiments such as four-wave mixing, as demonstrated in recent ultrafast holography experiments using blends of MEH-PPV and C<sub>60</sub>.<sup>5</sup> The results show that the early-time diffraction efficiency in the near-IR is dominated by a combination of phase (from  $\Delta n$ ) and amplitude (from  $\Delta\kappa$ ) gratings which arise from the complex  $\chi_{\text{inc}}^{(3)}$ , which, in turn, originates from the excited-state absorption. For such pulsed experiments where the pulsewidth is much shorter than the lifetime of the excited species, the change in the optical constants scales linearly with pulse energy, and  $\Delta n$  can be expressed as follows:<sup>20</sup>

$$\Delta n = \frac{39}{n_0^2} I_p \times \text{Re } \chi_{\text{inc}}^{(3)}, \quad (5)$$

where  $I_p$  is the pump intensity in kW/cm<sup>2</sup>,  $n_0$  is the ground-state index of refraction, and  $\chi_{\text{inc}}^{(3)}$  has units of (esu cm<sup>2</sup>/kW). The value of  $\chi_{\text{inc}}^{(3)}$  deduced from the holography measurement is  $\sim 10^{-8}$  esu, which is comparable to other robust nonlinear optical materials, such as semiconductor-doped glasses.<sup>22</sup>

In contrast to coherent nonlinearities,  $\chi_{\text{inc}}^{(3)}$  is inherently dependent on extrinsic parameters like the pulsewidth and photon energy. Thus, the measured value will in general depend on the conditions of the particular experiment. In the present case of low pump intensity and steady-state detection, we can relate the modulation of the index to the pump intensity by assigning  $\chi_{\text{inc}}^{(3)}$ , keeping in mind that in our system the response scales with the square root of the pump intensity (because of bimolecular recombination the lifetime of the excited state goes as  $I^{-1/2}$ ). For a pump intensity of 50 mW/cm<sup>2</sup> and ground state index of refraction of 1.9, the measured values of  $\Delta n$  imply  $\chi_{\text{inc}}^{(3)} \sim 2$  esu. This extraordinarily large value arises from the fact that  $\chi_{\text{inc}}^{(3)}$  is sensitive to the fluence; i.e., the flux integrated over the lifetime of the excited state.

#### V. CONCLUSION

We have measured the steady-state photo-induced absorption and photo-induced reflectance in films of MEH-PPV and BCHA-PPV blended with the fullerenes [5,6]PCBCR and C<sub>60</sub> from 0.05 eV to 1.9 eV. The spectral features observed at modest pump intensities are evidently due to efficient and long-lived electron transfer from the polymer to the fullerene. In the charge-separated state, both the positively charged polymer and the fullerene anion show absorption bands not present in the neutral state. These changes in absorption, measured by PIA, are coupled via the Kramers–Kronig relations to changes in the real part of the index of refraction,  $\Delta n$ , which we have measured by PIR. We find good agreement between  $\Delta n$  measured by PIR and the KK transformation of the PIA data, indicating that this approach to measuring nonlinear changes in the optical constants can serve as a valuable analytical tool for the characterization of

optical materials. The PIR measurement technique is quite robust and general, as is the relationship between absorption and refraction, and both can be applied in time domains ranging from steady-state to ultrafast.

The strong steady-state nonlinear optical response of the polymer/fullerene blends at low excitation density implies that the nonlinear optical response of these materials may be well suited for a variety of applications. Moreover, the spectral features observed in Figs. 1 and 2 provide information on specific spectral regions where, for example,  $\Delta n$  is large and therefore where large diffraction efficiencies are to be expected in picosecond dynamic holography.

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